

NADC - 80126 - 60



AD A116472

COMPOSITE REPAIR SYSTEM  
WITH LONG-TERM LATENCY

PREPARED BY  
JONAS WEISS

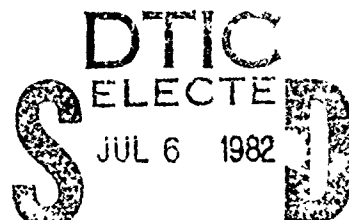
CIBA-GEIGY CORPORATION  
PLASTICS AND ADDITIVES DIVISION  
ARDSLEY, NEW YORK

FINAL REPORT  
NOVEMBER 1981

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PREPARED FOR  
NAVAL AIR DEVELOPMENT CENTER  
WARMINSTER, PENNSYLVANIA

CONTRACT NO. N62269 - 80 - C - 0711



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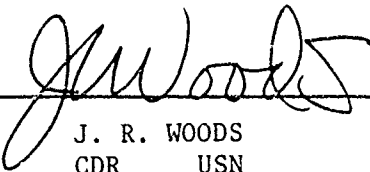
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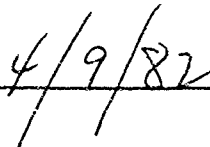
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## FOREWORD

This report was prepared by CIBA-GEIGY Corporation, Ardsley, N.Y., under contract NADC N62269-80-C-0711, "Composite Repair System with Long-Term Latency". It is the final technical report for the nine-month contract for the period October 27, 1980 to July 26, 1981. The program was sponsored by the Naval Air Development Center, Warminster, Pa. It was performed under the supervision of Mr. Ron Trabocco, contract monitor for NADC.

Performance of this contract is under the direction of the Plastics and Additives Research Department of CIBA-GEIGY Corporation. Dr. R. Seltzer is Associate Director and Dr. J. Weiss is Project Leader and principle investigator. Other major contributors to the project are H. Bouckris and W. Goldberg.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NADC 80126 - 60	2. GOVT ACCESSION NO. AD A116472	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Composite Repair System with Long-Term Latency		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT
7. AUTHOR(s) Jonas Weiss		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS CIBA-GEIGY Corporation Plastics and Additives Division Ardsley, N.Y. 10502		8. CONTRACT OR GRANT NUMBER(s) N62269-80-C-0711
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Air Development Center Warminster, Pennsylvania 18974		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS A510-5107/001-0/ 7W0625 0000
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE November 1981
		13. NUMBER OF PAGES 33
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 10, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Composite Repair      One-Part Epoxy Latent Epoxy Latent Hardener		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Novel latent epoxy hardeners which show promise for the field repair of composite structures of naval aircraft have been developed. At least one hardener is latent with epoxy resins for four to five months and exhibits good moisture resistance. These materials may provide the basis for a prepreg material to be used for the repair of graphite structural composites. (continued)		

Latent hardeners were prepared by reacting primary diamines with phthalic anhydride or phthalimide. These adducts are stable with multifunctional epoxy resins (MY 720 and 0510) at ambient temperatures and cure the resins at 150°C (302°F). DSC analyses show heats of reaction centered in the 101-120°C range, indicating that complete cures may be achieved at these lower temperatures. Initial studies show T<sub>g</sub>'s to be relatively high (120 to 146°C) and temperature/humidity resistance to be good.

A novel diamide, MXDAP, was synthesized from m-xylylenediamine and phthalic anhydride. It was thoroughly characterized as a 2:1 amine: anhydride adduct with amide and primary amine groups. Mixtures with MY 720 and 0510 are stable for four months at room temperature and are about 30% reacted after five months. The glass transition temperature was found to range from about 120 to 142°C for different samples and different methods of analysis. Almost clear buttons were made by compression molding at 150°C. These samples equilibrate at 5.5% water when kept at 71°C and 95% relative humidity. In comparison, moldings of MY 720 with DDS (diaminodiphenylsulfone) absorb 3.5% of their weight in water under the same conditions. The synthesis of MXDAP was scaled up to yield a batch of 280 grams of purified product.

Three other amine-anhydride adducts were synthesized by aqueous reaction with phthalimide, i.e. phthalamides of bis(p-amino-cyclohexyl)methane, 1,3-bis(aminomethyl) cyclohexane and 1,2-diaminocyclohexane. Initial studies show properties similar to that of MXDAP.

The mechanism of the latency of these materials was explained by analogy with HT 939, a CIBA-GEIGY latent hardener containing diethylenetriamine (DETA). HT 939 is incompatible with the standard epoxy resins, but becomes compatible on heating and reacts. Further heating releases free DETA, a very active curing agent. The amine adducts synthesized for this contract show promise of providing significantly better moisture resistance and high temperature properties than this DETA-derived product.

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## INTRODUCTION

This report describes the research under contract No. N62269-80-C-0711 to prepare and characterize a one-part resin system to be used in the field repair of graphite structural composites on naval aircraft.

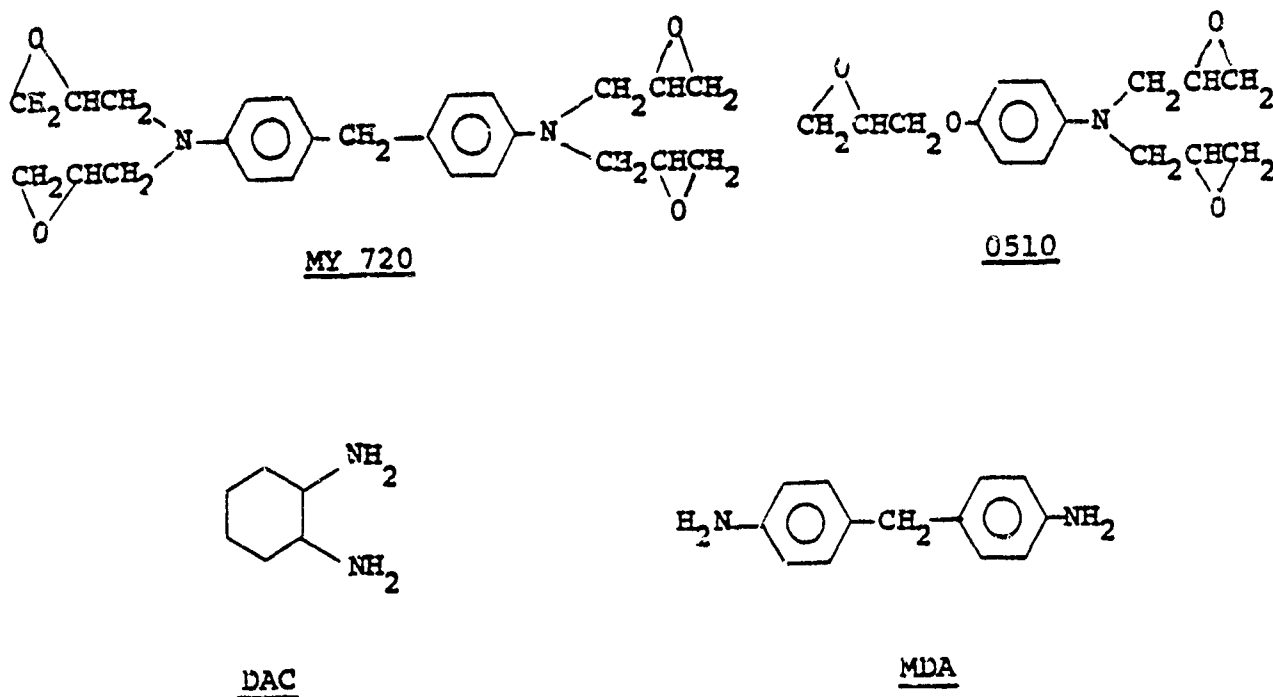
The resin should:

- 1) have long-term (at least six months) stability at ambient temperatures
- 2) cure in one hour at 121-149°C (250-300°F) using a heating blanket and mechanical pump
- 3) provide performance (e.g. high temperature properties and water resistance) similar to that of the resin used in the original advanced composite material. The basis for the matrix resin system of many of the composites for aircraft components is tetraglycidylated methylenedianiline (CIBA-GEIGY's MY 720) cured with bis-(p-aminophenyl)sulfone (Eporal or DDS). Because of the low reactivity of DDS at readily achieved temperatures, an accelerator, such as the complexed Lewis acid,  $\text{Et}_3\text{N} \cdot \text{BF}_3 \cdot \text{OEt}_2$ , is incorporated. Even with this accelerator, the MY 720/DDS system requires cure at high temperature (177°C or 350°F) and moderate pressure (100 psi) to insure full interaction between matrix and fiber reinforcement.

Although a repair system based on the MY 720/DDS matrix could provide properties equivalent to the advanced composite substrate, such a system is clearly unsuitable for field applications because of the high temperature and pressure necessary to fully cure and consolidate the system.

Work at CIBA-GEIGY done prior to this contract showed that an experimental two-part matrix resin system, Ca 79-4, (see Figure 1) is capable of meeting the cure and property requirements of a field repair system. The triglycidylated resin, 0510, lowers the viscosity of the MY 720 to a workable level. Diaminocyclohexane (DAC) provides a low-temperature cure while maintaining relative structural rigidity, and methylenedianiline (MDA) should improve high-temperature and water-resistance capabilities. DSC analysis of Ca 79-4 shows a double-peaked exotherm with maxima at 105°C (221°F) and 148°C (298°F), and indicates that the system can be cured readily within the parameters set in the NADC contract. The Tg of this system is very close to its final cure temperature. Unidirectional (24-ply) laminates were made with Thorne 300 and properties were compared with those of MY720/DDS laminates. Water absorptions for the two systems were similar. Short-beam-shear strengths of the laminates are given in Appendix I. The DDS-cured laminates gave higher strengths, but retention of strength after a two-week exposure to boiling water was equal or better for the Ca79-4 - cured laminates. Therefore, if this type of resin system can be made into a latent, one-part system, the requirements for a field repair matrix resin might be met.

Figure 1. Epoxy Resins and Amine Hardeners in the Ca 79-4 System



CIBA-GEIGY product HT 939 (see data sheet in Appendix II) already provides long-term latency for epoxy systems. This material is an amide produced by reacting phthalic anhydride and diethylenetriamine (DETA). It is latent with standard epoxy resins such as bisphenol-A diglycidyl ether (DGEBA). On heating to 150°C, it melts, rapidly gels and cures the resin. However, epoxies cured with this amine do not have good high-temperature and water-resistant properties.

From the above observations, the following objectives for the initial stages of this contract were formulated:

1. Determine the structure of HT 939 and its curing mechanism to serve as the basis for the preparation of analogous compounds.
2. Synthesize and characterize analogous compounds to HT 939, using higher-performance amines, e.g., aromatic diamines or relatively rigid aliphatic diamines (as in the Ca 79-4 system) and aliphatic diamines with aromatic character.

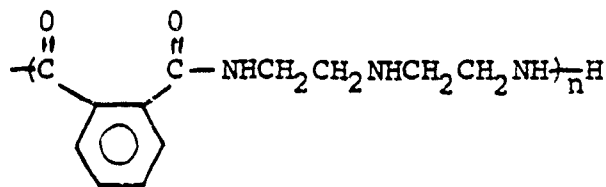
3. Combine these amine adducts with high-performance epoxy resins such as MY 720 and 0510 and study their stability at ambient temperatures.
4. Determine the reactivity and curing conditions for these systems.
5. Make test specimens of promising systems and determine properties, e.g., transition temperatures, water absorptions and mechanical properties, and compare with a standard MY 720/DDS system.

## Experimental Results and Discussion

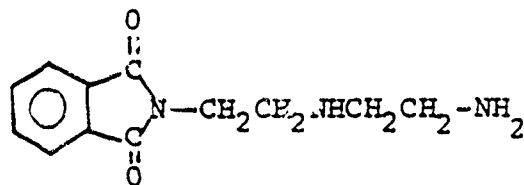
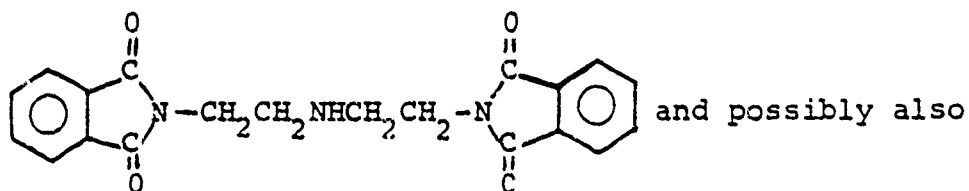
### A. Analyses of HT 939 and its Curing Mechanism

As noted in the introduction, HT 939 is a proprietary latent hardener synthesized from diethylenetriamine and phthalic anhydride. In order to serve as a model for the new latent hardeners to be synthesized for this contract, the structure and curing mechanism were determined.

Analyses were carried out via elemental determination, titration, thermogravimetric analysis, nuclear magnetic resonance (proton and C13) and infrared spectroscopy (IR). HT 939 was found to be an equimolar adduct of DETA and phthalic anhydride. It is a mixture of amides of the general structure shown below.



Titration shows that it contains 4.1 equivalents/kg of primary amine, which is consistent with the structure above for  $n = 1$ . Titration also showed about 0.95 equiv./kg secondary amine (lower than anticipated) and 0.25 equiv./kg of tertiary amine. It is a latent hardener for epoxies apparently because of its incompatibility (insolubility) with the resin. On heating to  $125^\circ\text{C}$  it melts, becomes soluble in the resin and starts the cure reaction. HT 939 releases DETA (identified by I.R.) when heated to  $150^\circ\text{C}$  and is converted to an imide, identified by NMR as probably



To determine the optimum hardener/epoxy stoichiometry, mixes of various ratios of HT 939 to MY 720 + 0510 (the epoxies in a 1:1 weight ratio) were made up and heats of reaction ( $\Delta H$ ) determined via differential scanning calorimetry (DSC). Also glass transition temperatures ( $T_g$ ) of the cured samples were determined by DSC and by thermomechanical analysis (TMA).

Results of the determination of the optimum stoichiometry for the HT 939-epoxy reaction are shown in Table II. Higher hardener/epoxy ratios gave greater low-temperature heats of reaction and generally higher  $T_g$ 's. However, blending of the formulation gets progressively more difficult at the higher ratios, so that the 0.85/1 ratio may be the best compromise between getting good properties and good processability.

Table I Effect of Stoichiometry on Properties of HT 939/MY 720/0510 Systems

HT 939/ MY 720 + 0510					
<u>Weight Ratio</u>	<u>Basis for Ratio</u>	$\Delta H, T_{peak}$ (kcal/Mole, °C)	$\Delta H_{Total}$ (kcal/Mole)	$T_g/DSC$ (°C)	$T_g/TMA$ (°C)
0.65	Technical literature	33.4 @ 11° 6.7 @ 280	55.8	132	107
0.85	Theory from structure	53.4 @ 107 17.7 @ 175	71.1	112	113
0.96	Total amine titration	53.4 @ 107 13.7 @ 170	67.1	110	108
1.15	Primary amine titration	59.8 @ 105 10.7 @ 170	70.5	129	124

A casting of HT 939 and MY 720 + 0510, postcured at 150°C, was tested for water resistance by immersion at 82°C. After six days it gained 27% in weight and became flexible. A DDS/MY 720 + 0510 casting absorbed only 5.6 weight percent under the same conditions. This result confirms the expected poorer resistance to water of HT 939-cured castings than those with higher-performance amines such as DDS. The water sensitivity and relatively low  $T_g$  of the HT 939 formulation confirm the need to develop a latent hardener with improved properties. Aromatic or other higher-performance amines, made latent in the same manner as in HT 939, may provide this improvement.

B. Synthesis and Characterization of New Latent Hardeners

Diamides of phthalic anhydride and the amines listed in Table II were made to provide curing agents analogous to HT 939.

Table II. Amines Used in Latent Curing Agent Syntheses

<u>AMINE</u>	<u>ACRONYM</u>	<u>SOURCES</u>
m-xylylenediamine	MXDA	Sherwin-Williams, Aldrich
1,3-bis(aminomethyl)cyclohexane	BAC	Sherwin-Williams
methylenedianiline	MDA	DuPont, Aldrich
bis(p-aminocyclohexyl)methane	PACM	DuPont, Pfaltz and Bauer
1,2-diaminocyclohexane	DAC	Pfaltz and Bauer

1. m-Xylylenediamine Phthalamide (MXDAP)

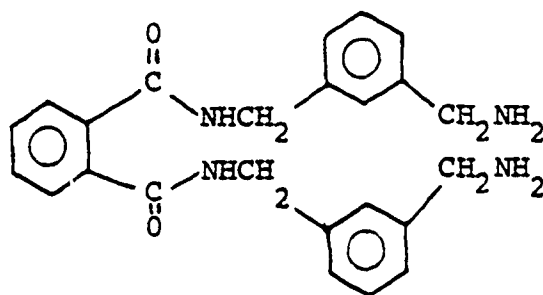
Numerous attempts were made to synthesize and purify the diamide of m-xylylenediamine (MXDAP). The following procedure was the most successful one.

A 20% dioxane solution of the anhydride was added dropwise to a refluxing (105°-125°C) solution of a 3-fold molar excess of the amine in dioxane solution (under nitrogen). Addition was completed in about 80 minutes and the mixture was heated for a total of 2 hours. The water of reaction and dioxane solvent were stripped under vacuum to yield a viscous liquid. This was triturated with successive portions of hot heptane, hot toluene, hexane and ethyl ether to produce solid material in about 70% yield. Analysis was by thin layer chromatography (TLC), infrared and nuclear magnetic resonance (NMR) spectroscopy, amine titration, elemental analysis and electrical conductivity. Table III shows some of these results.

Table III. Analysis of MXDAP

	<u>Theory</u>	<u>Found</u>
C	71.6%	69.9%
H	6.51%	6.53%
N	13.9%	14.1%
Total amine	4.97 eq./kg	5.01% eq/kg

The product obtained appears to be free of amine, imide and other impurities by chromatography and infrared spectroscopy and melts at 124-127°C. Elemental analysis, NMR and IR spectroscopy support the assignment of the 2:1 MXDA: anhydride amide structure shown below. There is some electrical conductivity in water and in methanol, but none in DMSO or in formamide, indicating the absence of ionic salt (e.g., amine carboxylate).

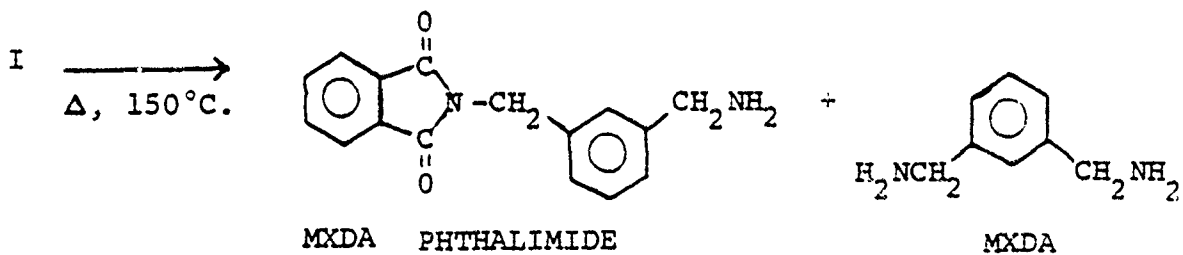


MXDAP (I)

NMR and infrared spectra are shown in Figures 2 and 3. Infrared analysis indicates that heating at 178°C converts the amide to imide and releases MXDA, as shown below. If the imidization occurs before the curing reaction, this would provide a secondary cure mechanism, and MXDAP would have three reactive amino groups instead of two. A DSC study to determine which stoichiometry gives a fuller cure was done; results are tabulated in Table IV. The heat of reaction at lower temperatures is much larger for the 4 equivalents/mole than for the 6 equivalents/mole stoichiometry. The total  $\Delta H$  is also higher for the mixture using 4 equivalents/mole. Apparently the amine/epoxy curing reaction occurs well before the imidization reaction.

Table IV. Stoichiometry of the MXDAP/Epoxy Reaction

<u>Stoichiometry of MXDAP Hardener</u>	<u>1st <math>\Delta H</math> (kcal/mole)</u>	<u>2nd <math>\Delta H</math> (kcal/mole)</u>
4 equiv./mole	69.8 @ 114°C	4.0 @ 206°C
6 equiv./mole	36.9 @ 117°C	17.6 @ 268°C



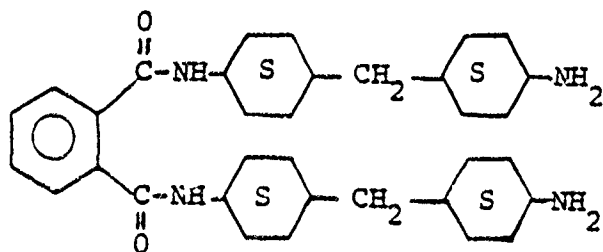
A larger batch of MXDAP was prepared at an addition temperature of 124°C to prevent the formation of precipitate. A very pale yellow waxy solid was obtained after evacuating at 2 mm and 50°C. Repeated triturations with diethyl ether, filtrations, grindings and reevacuations gave a 70% yield (280 grams) of a pale yellowish powder melting at 120-128°C. Its IR and NMR spectra are similar to that of the originally prepared material.

Synthesis via other procedures encountered various difficulties. A phthaloyl chloride addition to the amine gave an amide product contaminated with imide. A neat reaction with anhydride gave product which could not be purified easily. Reaction of the amine with phthalimide yielded some good product, but the procedure was not completely worked out.

## 2. PACM-20 Phthalamide (PACMP)

PACMP was prepared by the aqueous reaction of PACM-20 with phthalimide, according to a procedure similar to that published by Spring and Woods (J. Chem. Soc., 626, 1945). An emulsion of the amine in water was made using vigorous stirring. Phthalimide (from Aldrich) was finely ground and added to the emulsion at room temperature within a 10-minute period. The mixture was stirred for an additional 40 minutes and poured into a separatory funnel and extracted with chloroform. The chloroform solution was dried over magnesium sulfate, filtered and stripped. The product was washed with hexane and with anhydrous ethyl ether and then stripped in a vacuum oven.

A glassy, low melting (75-90°C) material was isolated in 28% yield. Infrared analysis (Figure 4) showed a strong amide absorption, with only a trace of imide and no amine salt. NMR analysis (Figure 5) was consistent with the 2:1 adduct structure shown below.



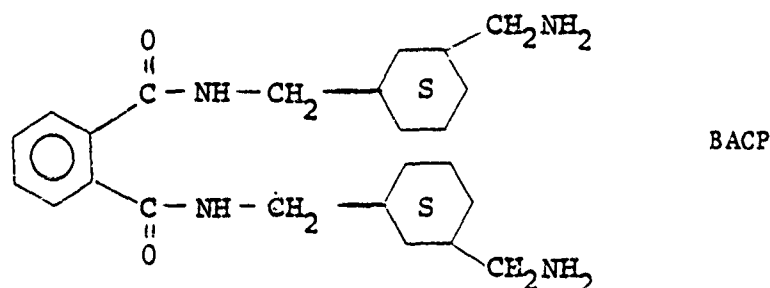
PACMP



The procedure used to prepare MXDAP was not successful with PACMP. The addition of phthalic anhydride to a dioxane solution of duPont's PACM-20 yielded a solid with a wide melting range which was apparently a mixture of compounds and which contained amine carboxylate salt. A synthesis using Pfaltz and Bauer's higher melting isomer mixture of 4,4'-diaminodicyclohexyl methane yielded a purer product, but the elemental analysis and acid-base titration did not agree with the 2:1 adduct structure indicated by NMR. A similar preparation using the Pfaltz and Bauer isomer mixture and reacting in an aqueous THF solvent gave a very low yield of product.

### 3. BAC Phthalamide (BACP)

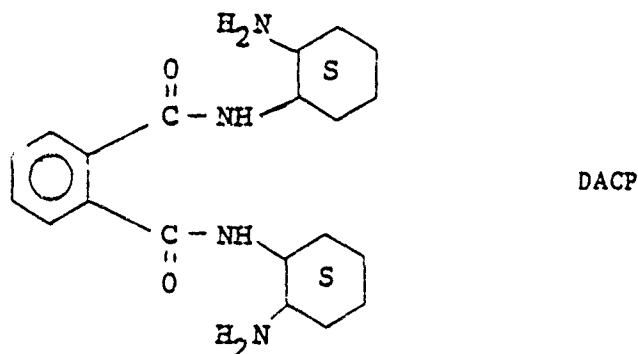
The aqueous phthalimide procedure described for the preparation of PACMP gave the best results with 1,3-bis(aminomethyl) cyclohexane. A 20% yield of a low-melting (54-66°C) glassy product resulted. IR analysis, shown in Figure 6, shows amide absorption with no imide or salt contamination. NMR analysis (Figure 7) supports the 2:1 adduct structure shown below.



BACP made by the dioxane solution method gave a mixture of 2:1 and 1:1 adducts (by NMR and by amine titration) and contained some amine carboxylate salt.

### 4. DAC Phthalamide (DACP)

1,2-Diaminocyclohexane was reacted with phthalimide in an aqueous medium according to the procedure used for PACMP and BACP. This gave a 16% yield of a light tan water-soluble solid melting at 68 to 75°C. The IR spectrum (Figure 8) shows amide absorption, a trace of imide and no salt peaks. An NMR spectrum (Figure 9) indicates the structure is a 2:1 adduct, shown below.



1,2-Diaminocyclohexane reacted with phthalic anhydride in dioxane (as in previous preparations) yielded an amine carboxylate salt and other products, including a 1:1 amine:anhydride adduct.

5. MDA Phthalamide

Most of the methylenedianiline used in a reaction with phthalic anhydride in dioxane was recovered unreacted. The amide product could not be separated from the solid amine.

The aqueous procedure to synthesize the phthalamide of MDA was also tried. The aqueous slurry of MDA was very thick and no apparent reaction took place with finely powdered phthalimide. Warming the mixture to 45°C did not change this situation. Apparently the insolubility of MDA in water precluded any reaction with phthalimide.

C. Determination of Reactivity and Latency

Epoxy resins MY 720 and 0510 were mixed in a 1:1 weight ratio, and an equivalent amount of the diamide hardeners were added to the formulation, assuming that one mole of adduct will react with four epoxy groups (as found in the HT 939 work). The resulting paste was analyzed via DSC and also probed with a spatula. The material was stored at room temperature and reanalyzed to detect any changes, e.g., in color, flow and heat of reaction at regular intervals.

Similar work was done using a mixture of MY 720 and the latent amines, without any 0510 resin.

1. Reactivity and Latency of MXDAP Formulations

DSC analysis (Figure 10) of a paste of MXDAP (I, p.12), MY 720 and 0510 showed a large low-temperature exotherm (69.8 kcal/mole epoxy resin centered at 114°C), indicative of a complete curing reaction and a small, high-temperature exotherm (4.0 kcal/mole with a peak at 206°C). The room-temperature stability (latency) of this formulation was determined by subsequent DSC analyses at regular intervals, shown in Table V.

Table VChange in Reactivity of MXDAP/MY 720/0510 with Time at Room Temperature

<u>Time Elapsed (Weeks)</u>	<u><math>\Delta H</math> (kcal/mole)</u>	<u>% of Original Value</u>
0	69.8	-
2	68.7	98.5
7	67.3	96.5
11	66.5	95.3
16	58.7	84.1
21	45.6	65.3
27	37.9	54.3

The heat of reaction is virtually unchanged (within experimental error) for eleven weeks, drops to about 84% of the original value at sixteen weeks and is considerably lower at six months. No gross changes in the formulation (e.g. color and flow) were noted after five months at ambient temperatures, but after six months the material was noticeably advanced. A useful room-temperature shelf life for this material seems to be about four months.

DSC analysis of a similar formulation using only MXDAP and MY 720 gave similar results: a 86.4 kcal/mole exotherm centered at 118°C and a 1.6 kcal/mole exotherm with a peak at 220°C. These analyses indicate that a full cure can be expected with MXDAP at temperatures as low as 120°C.

## 2. Reactivity and Latency of Hardener/Epoxy Mixtures

The new latent hardeners were mixed with MY 720, or with MY 720 plus 0510, to make pastes. These were then analyzed via DSC to determine heats of reaction and to determine the period of their stability at ambient laboratory temperatures ( $\sim 68-76^{\circ}\text{F}$ ). The results are given in Table VI.

Table VI. Heats of Reaction and Stability of Hardener/Epoxy Mixtures

<u>Latent Hardener</u>	<u>Epoxy Resin(s)</u>	<u>1st <math>\Delta H</math> (kcal/mole) &amp; Peak T</u>	<u>2nd <math>\Delta H</math> (kcal/mole) &amp; Peak T</u>	<u>Period of Stability</u>
HT 939	MY 720/0510	53.4 @ $107^{\circ}\text{C}$	17.7 @ $175^{\circ}\text{C}$	>6 months
MXDAP	MY 720/0510	69.8 @ $114^{\circ}\text{C}$	4.0 @ $206^{\circ}\text{C}$	4-5 months
MXDAP	MY 720	86.4 @ $118^{\circ}\text{C}$	1.6 @ $220^{\circ}\text{C}$	-
PACMP	MY 720/0510	38.7 @ $115^{\circ}\text{C}$	20.0 @ $272^{\circ}\text{C}$	2-4 weeks
PACMP	MY 720	35.9 @ $120^{\circ}\text{C}$	5.6 @ $222^{\circ}\text{C}$	-
BACP	MY 720/0510	29.7 @ $101^{\circ}\text{C}$	19.4 @ $227^{\circ}\text{C}$	>2 weeks
DACP	MY 720/0510	29.7 @ $105^{\circ}\text{C}$	9.0 @ $222^{\circ}\text{C}$	>2 weeks

None of the other latent hardeners show as full a cure as with MXDAP. This may be due to a non-optimum hardener to epoxy ratio, or to incompatibility of the reactants. Work to improve these conditions to get a higher  $\Delta H$  would be useful. However, a cure at about  $150^{\circ}\text{C}$  may be sufficient to determine physical properties of test pieces, since Tg's (Table VII) indicate that crosslinking is extensive.

#### D. Properties of Cured Epoxy Systems

Attempts to prepare castings for mechanical property measurements from MY 720/0510 and the latent hardener candidates were unsuccessful. Pouring a well-mixed slurry of the components between teflon covered plates and curing at temperatures up to 150°C produced opaque and heterogeneous samples. In contrast to HT 939, with standard casting techniques, these higher performance hardeners do not dissolve in the resin prior to cure. It was decided to optimize the materials for the project before working on a process to make test samples for tensile testing.

However, almost clear, brown, one-inch-diameter discs were made from MXDAP, MY 720 and 0510 by compression molding at 6,000 psi and 150°C for 30 minutes. After postcuring at 150°C, these samples were used for water absorption studies at 71°C and 95% relative humidity and the determination of T<sub>g</sub> by means of TMA.

Comparison of glass transition temperatures of epoxy resins cured with DDS, HT 939, MXDAP, PACMP and BACP are shown in Table VII. Multiple values given are for different samples. Water absorption at 71°C and 95% relative humidity is also reported.

Table VII. Cured Epoxy Properties

<u>Formulation</u>	<u>Final Cure Temp. (°C)</u>	<u>T<sub>g</sub>/TMA (°C)</u>	<u>T<sub>g</sub>/DSC (°C)<sup>c</sup></u>	<u>Water Absorption (%)<sup>a</sup></u>
MY 720/DDS	200	232	-	3.5
DGEBA/DDS	200	155	-	-
DGEBA/HT 939	150	90	-	-
MY 720/0510/HT 939	150	113, 120	112	(b)
MY 720/0510/MXDAP	150	120, 142	120, 130	5.5
MY 720/0510/PACMP	-	-	146	-
MY 720/0510/BACP	-	-	145	-
MY 720/0510/DACP	150	140	120	-

(a) saturation after exposure at 71°C/95% R.H.

(b) becomes flexible after immersion at 82°C.

(c) after brief heating to 180°C in DSC apparatus.

Glass transition temperatures for MXDAP-cured epoxy resins (by TMA and by DSC) ranged between 120 and 142°C. Differences may be due to incompatibility of the reactants, which can cause irreproducibility in their cure. There is also a very small transition at about 80°C (see Figure 11 for the TMA scan).

The glass transition temperatures for MY 720/0510 cured with DACP was found to be close to the final postcure temperature of 150°C. Using DSC, which involves first heating the uncured mix up to about 180°C, Tg's for MY 720/0510 cured with PACMP or with BACP were about 145°C. These systems also had smaller lower-temperature transitions.

Water pick-up on an eighth-inch thick molding of MXDAP/MY 720/0510 was 5.5 wt. % at equilibrium. A casting of MY 720/DDS under the same conditions absorbs an equilibrium amount of 3.5% of its weight in water after two weeks. Work on the effect of water pick-up on Tg was complicated by the loss of water while running the tests. Pressure cell DSC to alleviate this problem was begun but has not yet been completed.

## CONCLUSIONS

Four new latent epoxy hardeners have been prepared. The phthalamide of m-xylylenediamine was well characterized by IR, NMR, titration and reactivity with epoxy groups. MXDAP is latent with MY 720 and 0510 for four months at ambient temperatures and provides a full cure at 150°C. It was made reproducibly from a relatively inexpensive and available diamine. Moldings using MXDAP show good temperature/humidity resistance; water absorption was 5.5%, vs. 3.5% for an MY 720/DDS control. Tg was found to range between 120 and 142°C for various determinations; incompatibility of components may account for the differences found.

Phthalamides of PACM-20, BAC and DAC were also made and characterized. They cure epoxy resins at temperatures of 150°C or below and yield Tg's (measured by TMA) up to 140°C, when postcured at 150°C. Latency of mixtures with MY 720 and 0510 is at least two weeks and these studies are continuing.

Determination of physical properties of cured epoxy resins has been delayed by the difficulty of making test samples, since low flow and incompatibility of components caused castings to be heterogeneous.

The mechanism of epoxy curing using HT 939 was elucidated. Despite the presence of primary amine groups, no reaction occurs at room temperature because of the incompatibility of the components. Heating solubilizes the hardener and converts it to an imide plus a free amine, which then reacts with the epoxy groups. As expected for diethylene triamine-cured epoxides, water resistance is low. The phthalamides of MXDA, PACM-20, BAC and DAC seem to be similar to HT 939 in their reactions with MY 720 and 0510. They provide higher Tg's (120 to 146°C vs. about 113°C for HT 939) and MXDAP gives better water resistance than HT 939. Therefore, the new phthalamides are good candidates for a curing agent in a latent composite repair system.

# RECOMMENDATIONS

The nine months of contract work described has focused on the preparation of candidate latent hardeners and their preliminary evaluation. In a successive contract period, we propose to determine the properties of cured resins and composites. Specifically, we recommend:

1. Modification of the epoxy resin system to improve compatibility with the latent hardeners and allow the preparation of test samples for the determination of various physical properties. For example, MY 720 will be partly replaced with a less viscous or more compatible resin.
2. Modification of the latent hardeners by grinding to a finer particle size to improve compatibility.
3. Determination of optimum hardener/epoxy ratios.
4. Preparation of test samples, e.g., "dog bones" for tensile tests.
5. Determination of mechanical properties of cured samples and comparison with those of currently used materials.
6. Study of the effect of high humidity exposure on Tg, using pressure cell DSC. (This study has been started, but no results are available yet.)
7. Development of the most promising formulation into a graphite prepreg suitable for field repairs.
8. Evaluation of prepreg properties, especially the low-pressure (vacuum bag) curing of the system.
9. Optimization of prepreg properties by modification of its components.

Also, a repair product with a precured laminate and a latent epoxy resin system as an adhesive may be developed.



FIGURE 2. IR SPECTRUM OF m-XYLYLENEDIAMINE PHTHALAMIDE

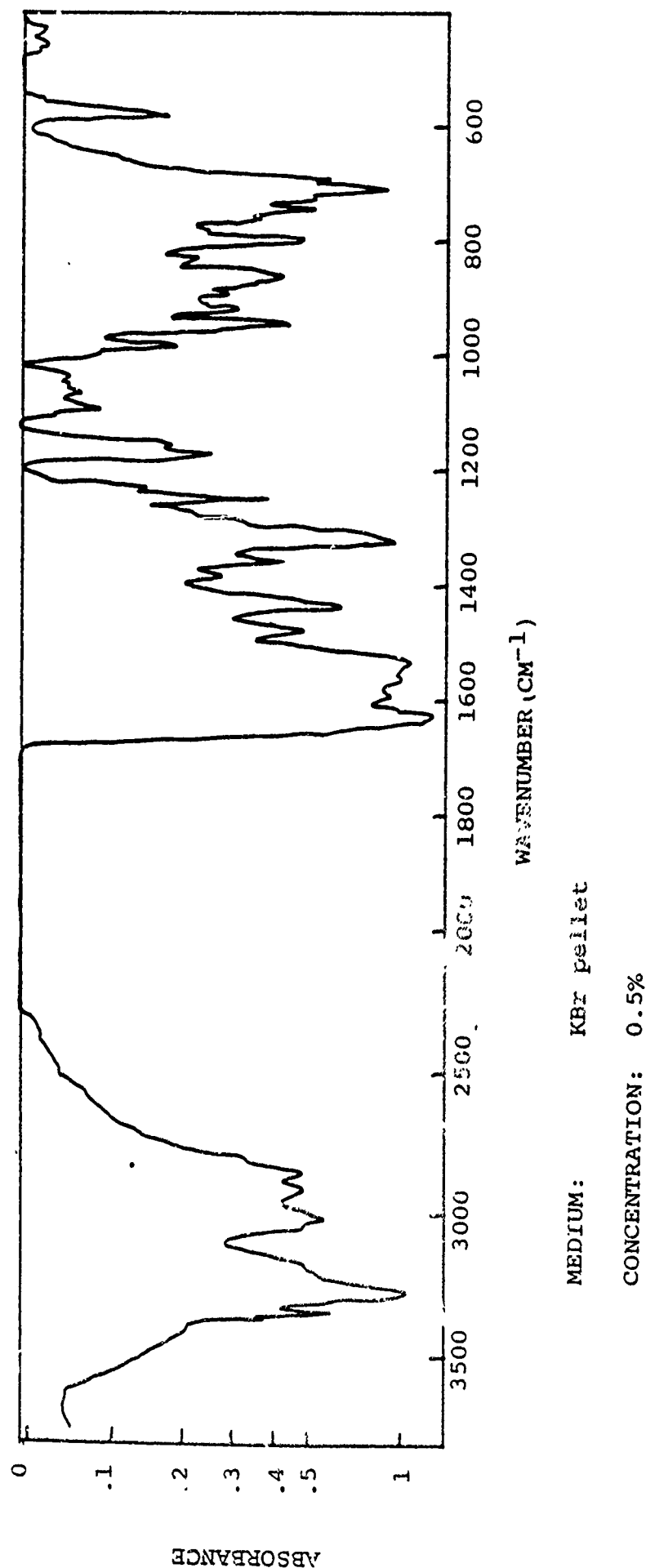
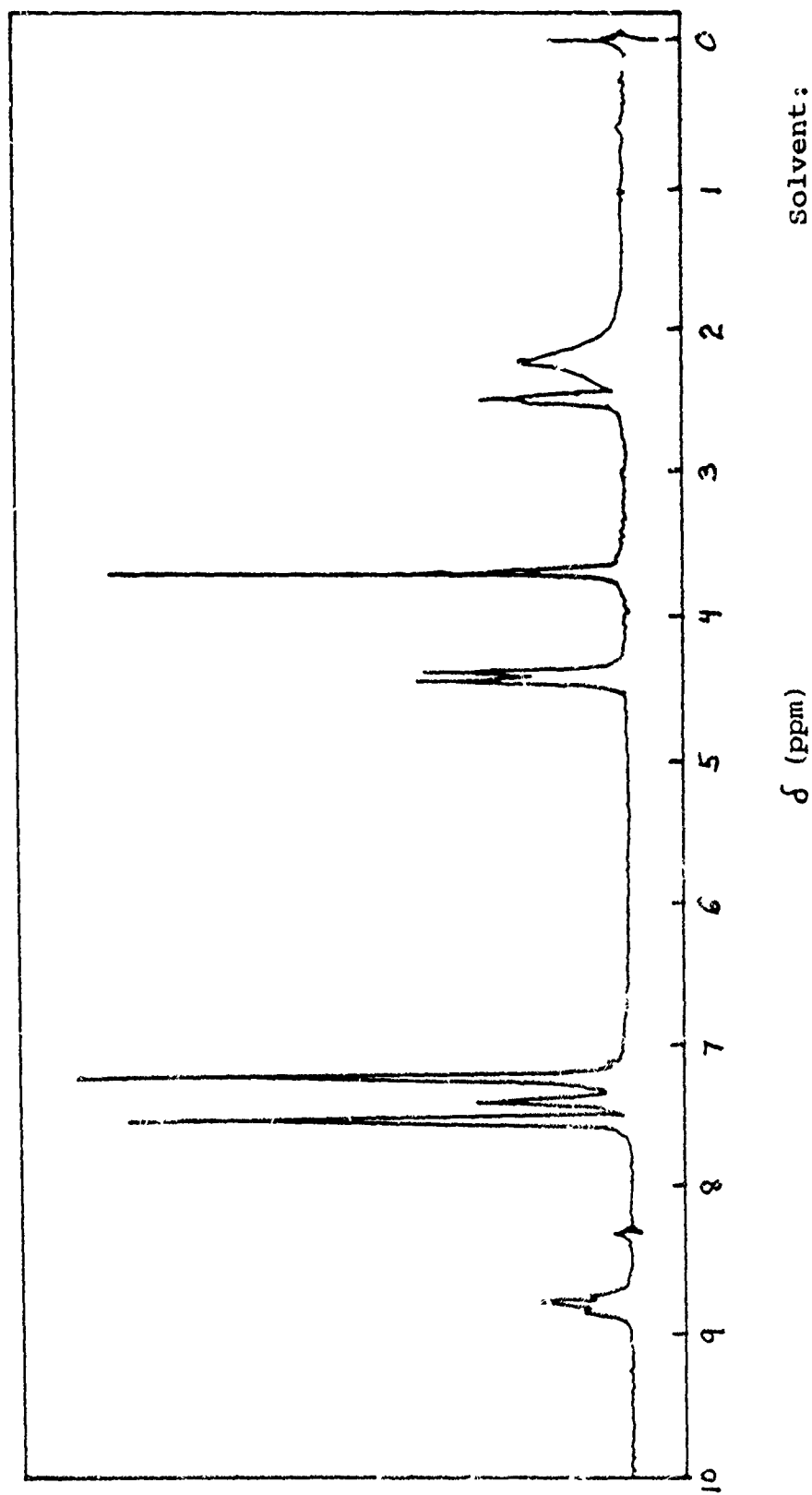
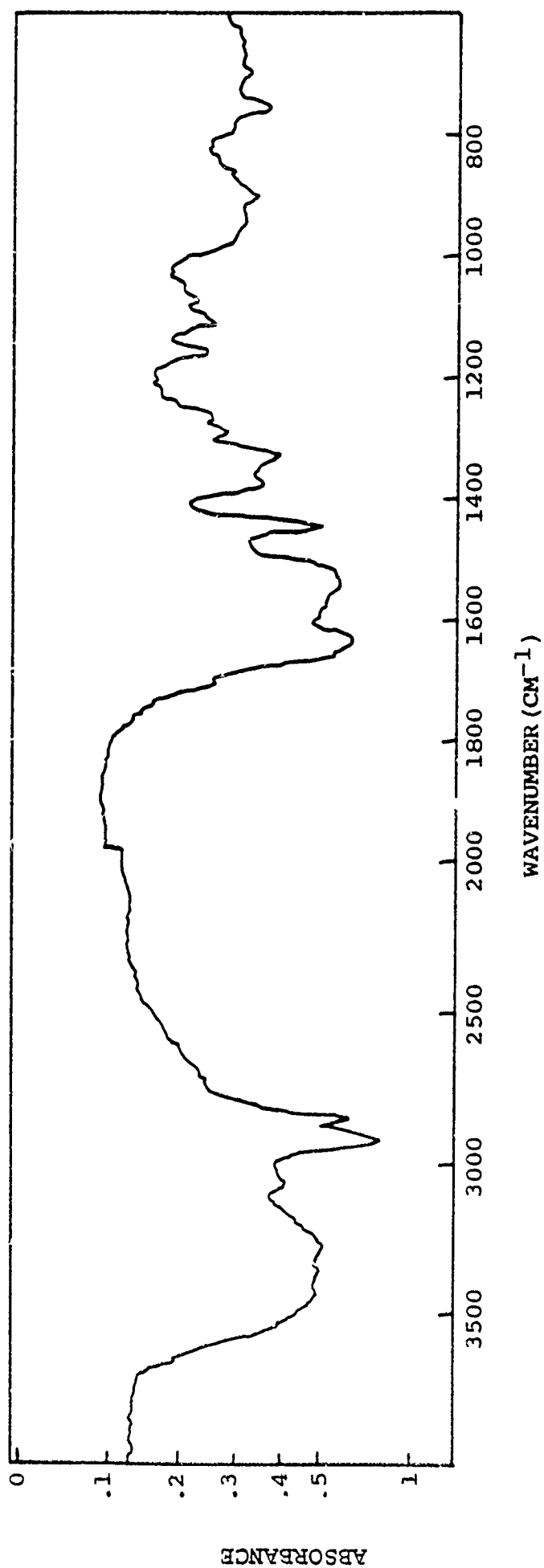


FIGURE 3. NMR SPECTRUM OF m-XYLYLENEDIAMINE PHTHALAMIDE



Solvent: DMSO- $d_6$   
Temperature: Ambient  
Reference: SiMe $_4$

FIGURE 4. IR SPECTRUM OF PACM-20 PHTHALAMIDE



MEDIUM: KBr pellet

CONCENTRATION: 0.5%

FIGURE 5. NMR SPECTRUM OF PACM-20 PHTHALAMIDE

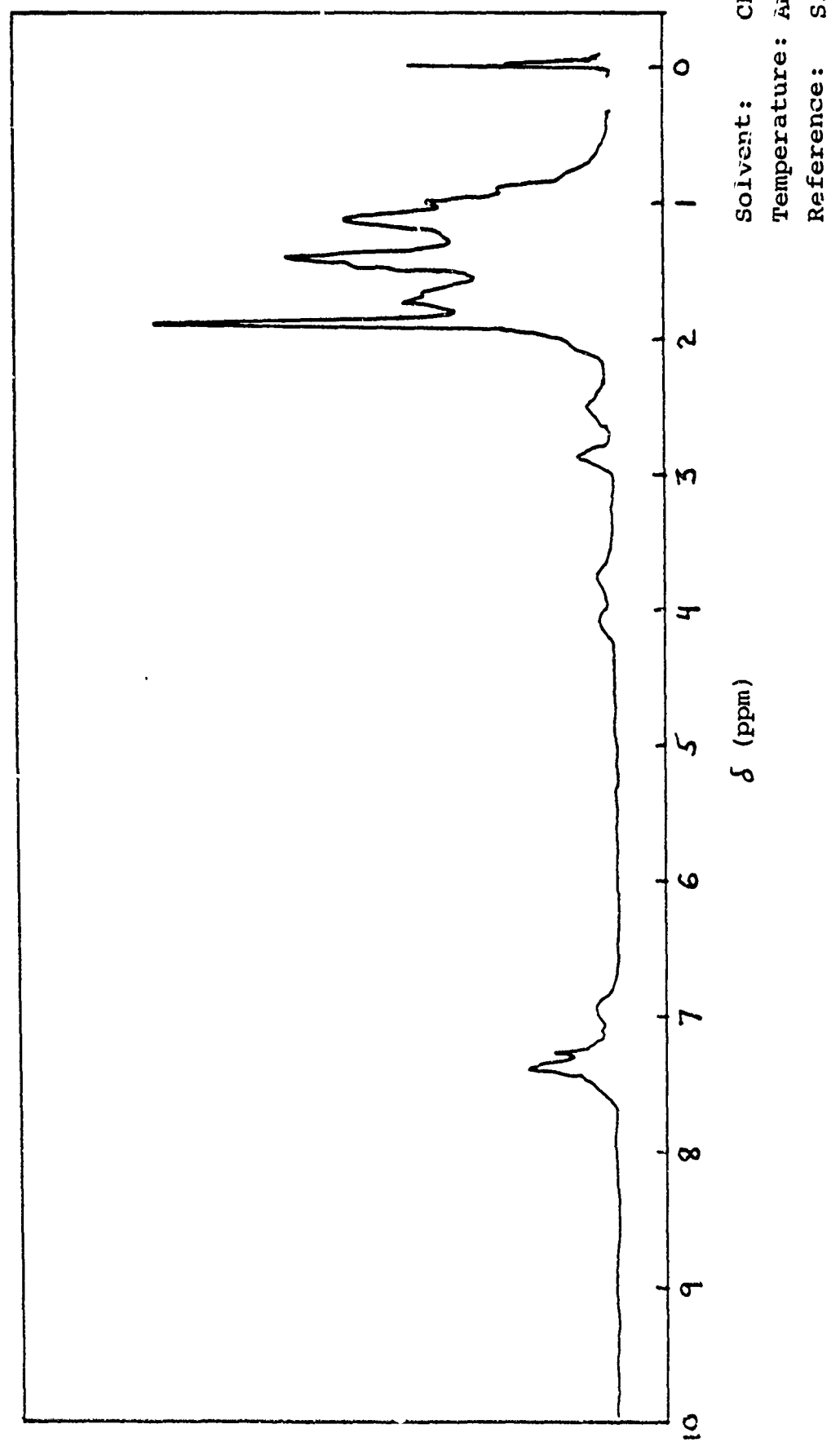
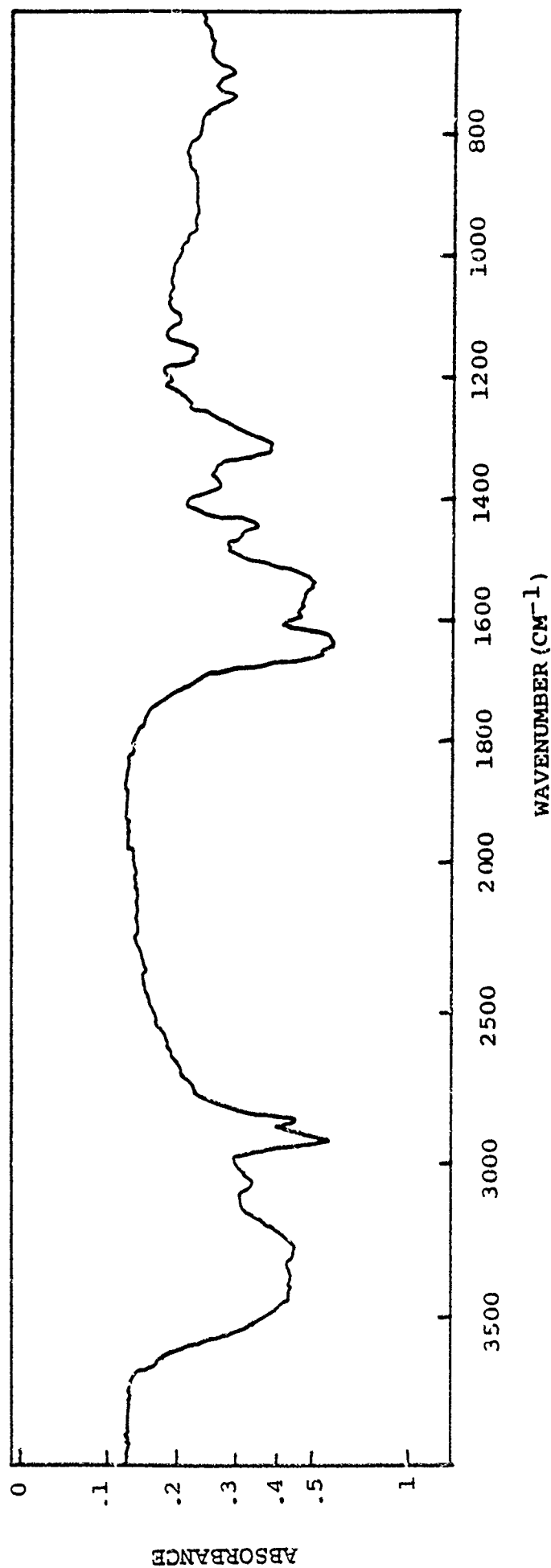


FIGURE 6. IR SPECTRUM OF BAC PHTHALAMIDE



MEDIUM: KBr pellet

CONCENTRATION: 0.5%

FIGURE 7. NMR SPECTRUM OF BAC PHTHALAMIDE

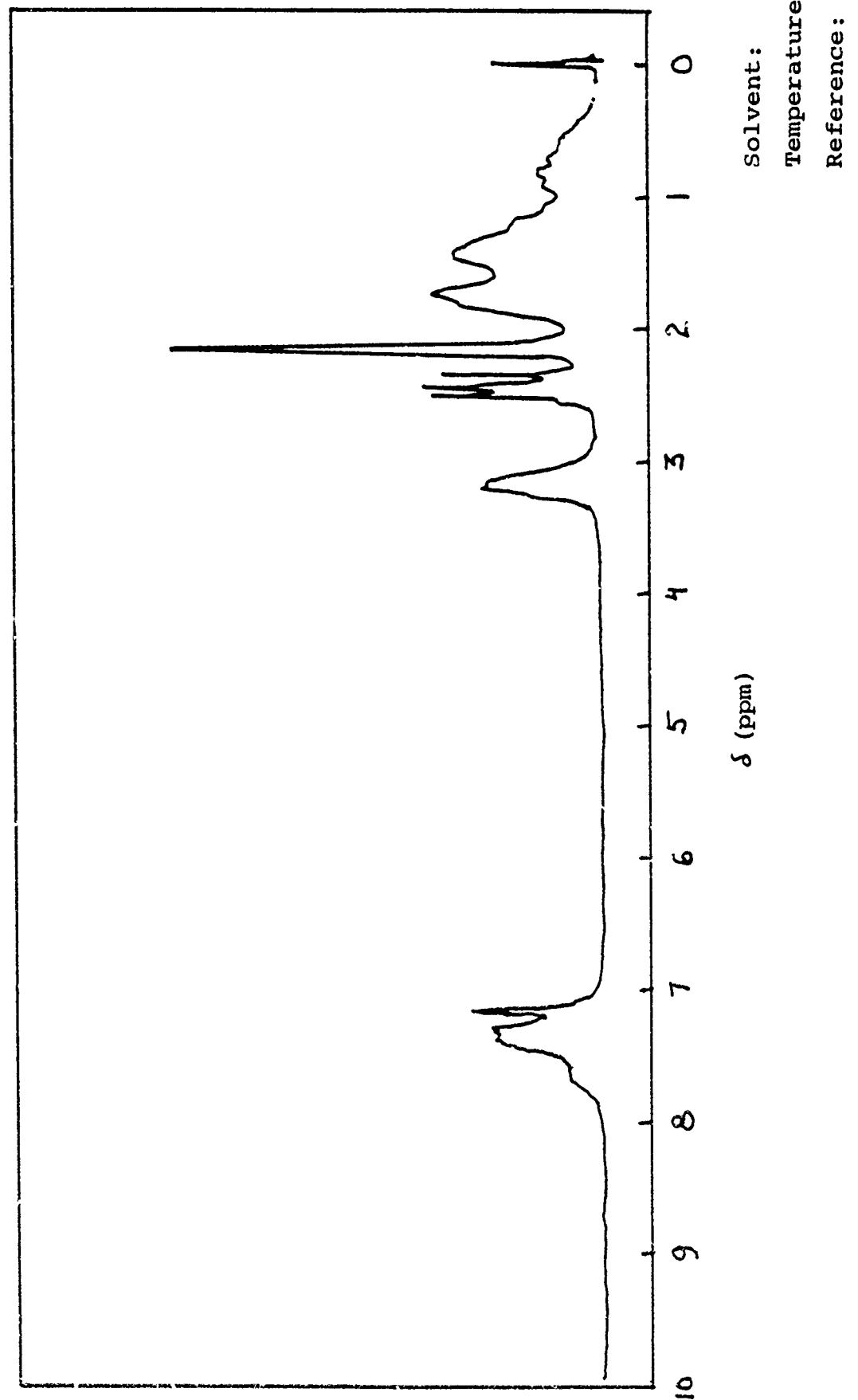
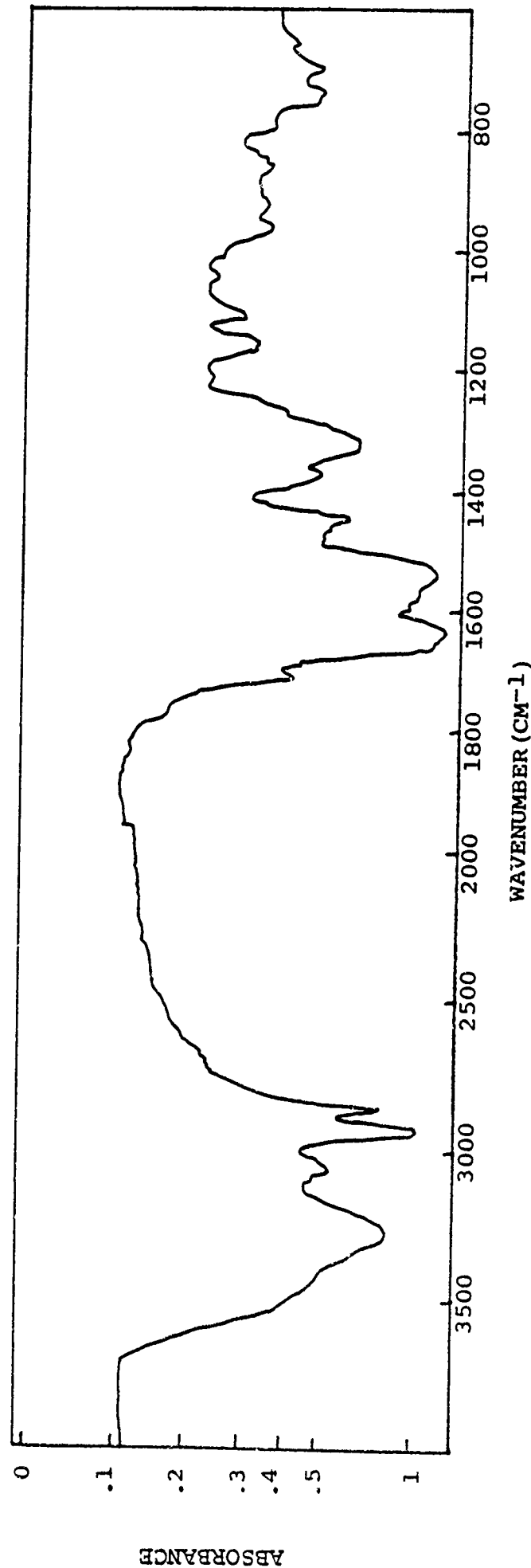


FIGURE 8. IR SPECTRUM OF DAC PHTHALAMIDE



MEDIUM: KBr pellet

CONCENTRATION: 0.5%

FIGURE 9. NMR SPECTRUM OF DAC PHTHALAMIDE

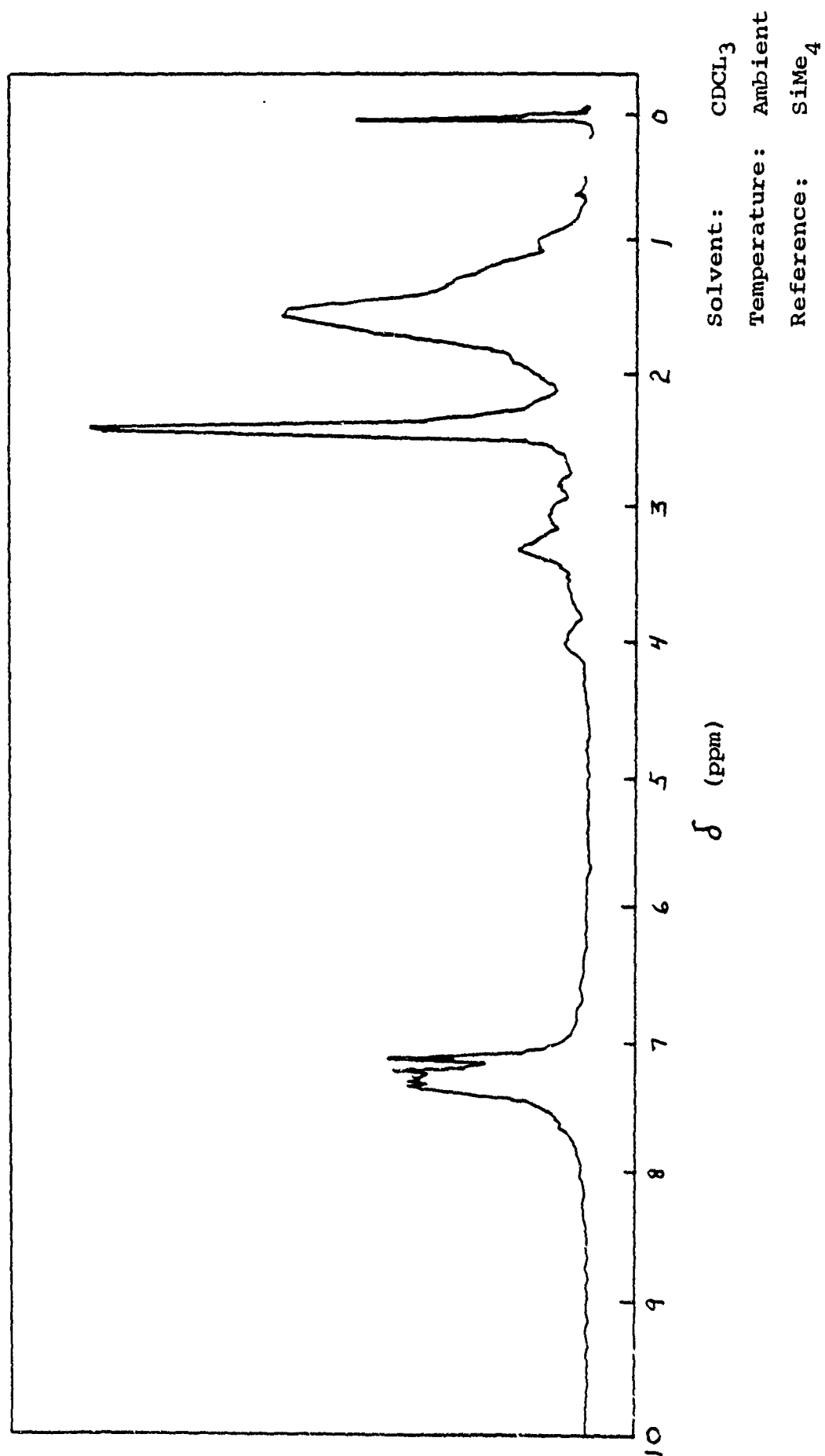




FIGURE 10. DSC SCAN OF MY 720/0510/MXDAP

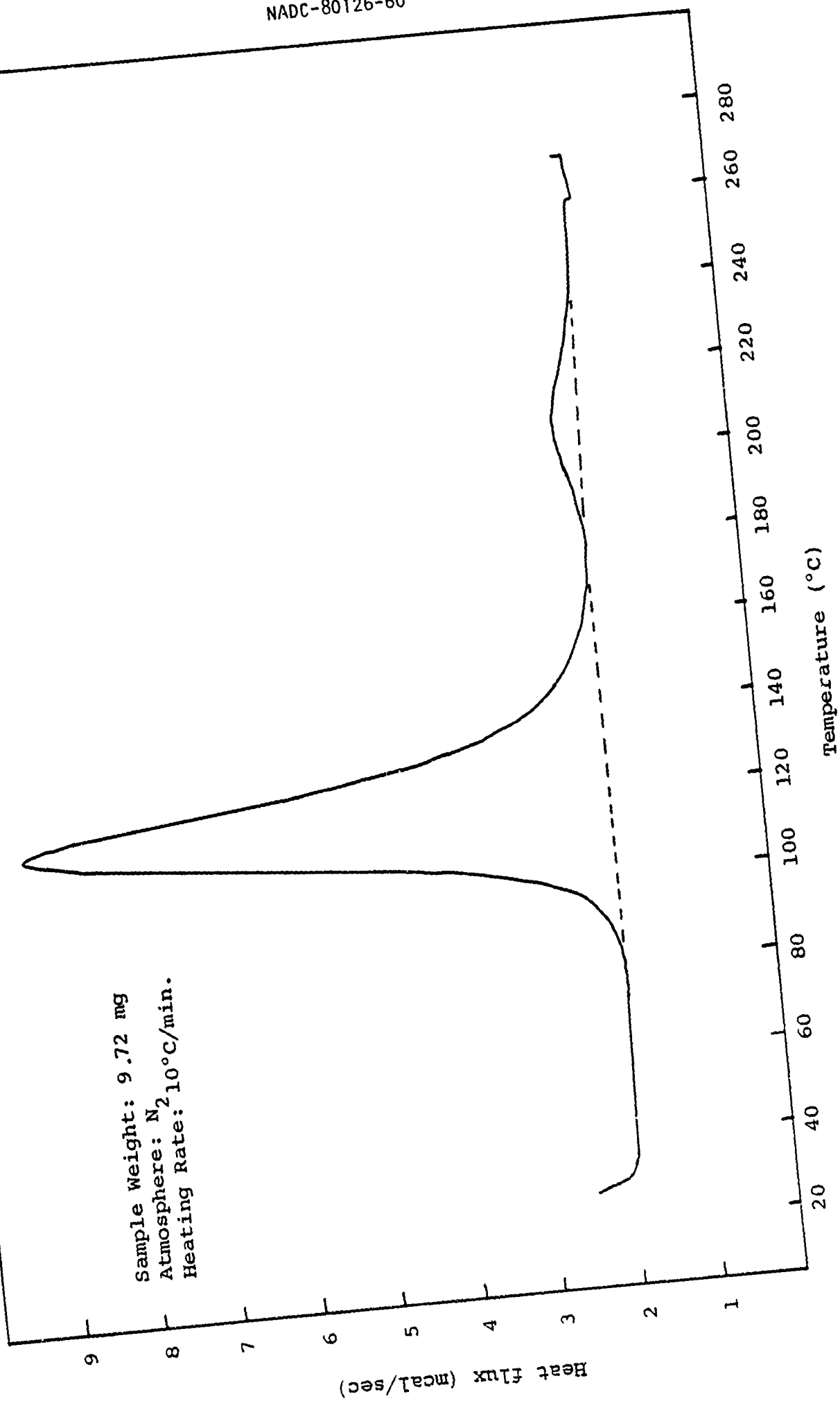
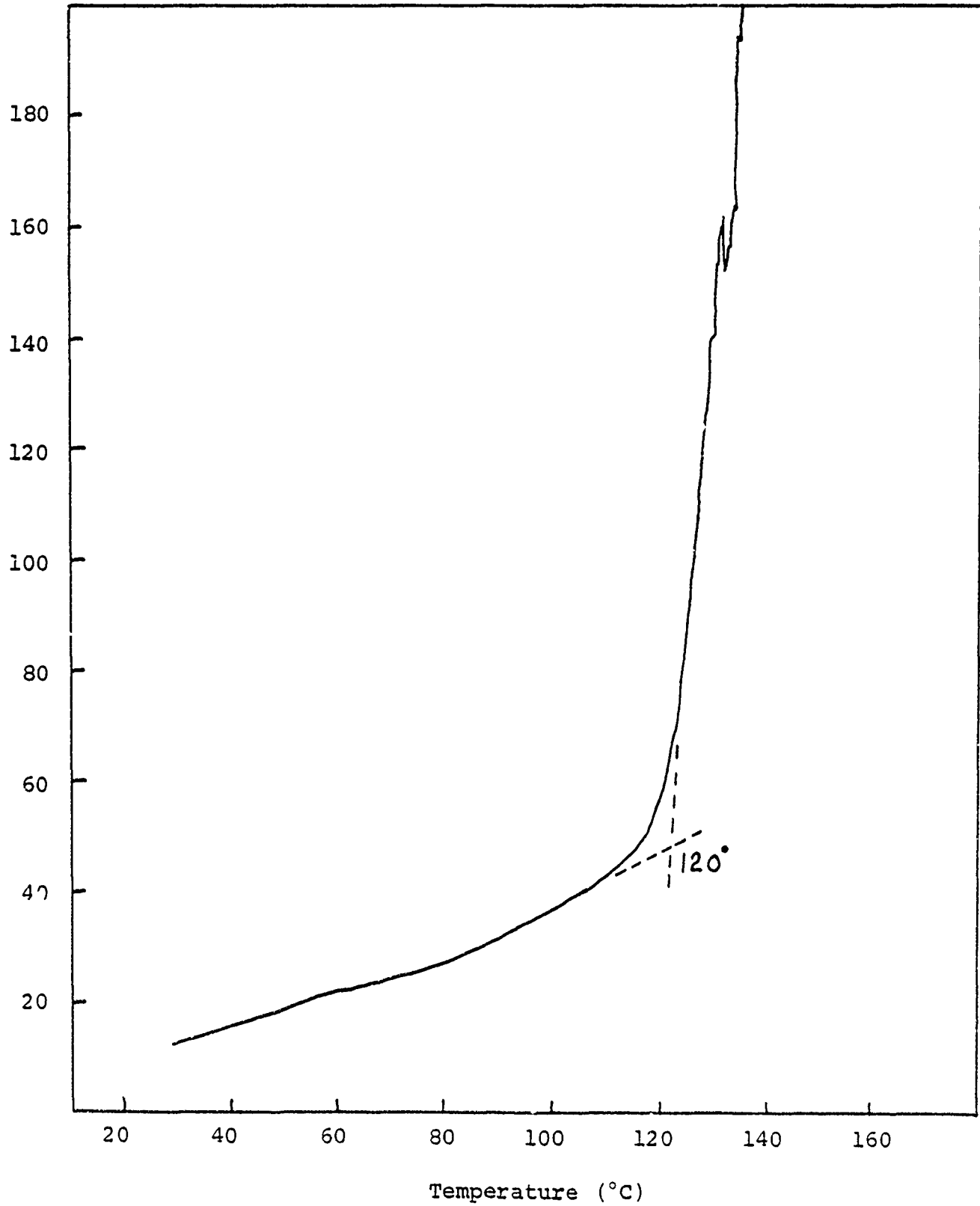


FIGURE 11. THERMOMECHANICAL ANALYSIS OF MXDAP/MY 720/0510 MOLDING

ATM: N<sub>2</sub>

Heating rate: 5°/min.

Sample size: 5.92 mm



APPENDIX I. Properties of Ca 79-4 Epoxy/Thornel 300 LaminatesTable VIII. Short-Beam-Shear Strength of Laminates Before and After Boiling-Water Exposure to Saturation

Test Temperature	<u>Strength Before Exposure</u> <u>(kg/mm<sup>2</sup>)</u>		<u>Strength After Water Boil</u> <u>(kg/mm<sup>2</sup>)</u>	
	<u>MY 720 System<sup>a</sup></u>	<u>Ca79-4 System<sup>b</sup></u>	<u>MY 720 System<sup>a,c</sup></u>	<u>Ca79-4 System<sup>b,d</sup></u>
25	11.9	10.3	8.7	6.7
50	11.2	9.3	7.9	6.0
80	10.2	8.2	7.2	5.3
104	9.5	7.2	6.6	4.6
121	8.7	4.5	4.5	4.2

a) 26.5% resin

b) 28.8% resin

c) 2.1% wt. gain at saturation

d) 2.3% wt. gain at saturation.

APPENDIX II. HT939 Data Sheet

Type: Modified Polyamide based on Diethylenetriamine and  
Phthalic Anhydride

Typical Properties

Appearance: Pale yellow, fine powder

Softening Point: 105°C

Equivalent Weight: 93 g.

Storage: Hygroscopic - Store under dry conditions

Sample Formulation

ARALDITE 6010 - 100 pbw + HT939 - 35 pbw

Viscosity of Mix: 1200 poise at 25°C

Viscosity after 6 months at 25°C: 1100 poise at 25°C

Stability at Room Temperature: >6 months

Gel Time: 5 minutes at 100°C

Cure Schedule: Gel at 90°C + 3 hours at 150°C

Typical Properties of Cured Formulation with ARALDITE 6010

Deflection Temperature: 97°C

Tensile Strength: 809 kg/cm<sup>2</sup>

Tensile Elongation: 4.6%

Tensile Modulus: 35,000 kg/cm<sup>2</sup>

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